10/509071
DT09 Rec'd PCT/PTO 24 SEP 2004

Process for preparing functionalized polyorganosiloxane resins by redistribution in the presence of at least one derivative of triflic acid

The field of the invention is that of the production of silicone or polyorganosiloxane resins, referred to hereinbelow as POS resins. The POS resins more especially targeted are those comprising siloxyl units M: ($R_3SiO_{1/2}$) and optionally D: ($R_2SiO_{2/2}$) and/or T: ($RSiO_{3/2}$), said resins moreover being functionalized, i.e. they comprise units M': ($Y_aR_{3-a}SiO_{1/2}$) and optionally D': ($RYSiO_{2/2}$) and/or T: ($YSiO_{3/2}$); Y representing in these formulae a functional group, for example a hydrogen or a vinyl, R a hydrocarbon-based group and a = 1 or 2.

These functional silicone resins MQ may be liquid or solid at room temperature. They have been known for a very long time and are currently used in many applications, for instance in electrical insulating varnishes, heat-resistant coatings, encapsulating materials for semiconductor components, etc.

The functional MQ POS resins (MM'Q) whose production forms the subject of the present invention may also comprise siloxyl units D and/or T, or even

functionalized siloxyl units D′ and/or T′.

The main routes of access to functional MQ resins are currently processes of condensation/-hydrolysis starting with sodium silicate or alkyl silicate (US-B-2 676 182, US-B-2 814 601, US-B-2 857 356, US-B-4 707 531). These techniques are not without drawbacks, especially in terms of ease of use, cost and production of ecotoxic and/or hazardous effluents.

However, an alternative, which is attractive in principle, to these condensation/hydrolysis techniques exists, namely the redistribution of POS oils in a POS resin comprising MQ units.

By way of illustration of this route of functionalization of resins of MQ type by redistribution, mention may be made of US-B-4 774 310, US-B-5 494 979 (≈ EP-A-0 617 094) and US-B-5 510 430.

Patent US-B-4 774 310 describes the preparation of Si-H functionalized resins by redistribution of tetramethyldisiloxane (M'_2) in an MQ resin dissolved in an organic solvent, in the presence of triflic acid or perfluoroalkanesulfonic acid (TFOH). The reaction medium is heated to a temperature of between 50 and 100°C and the triflic acid catalyst is then neutralized with $NaHCO_3$. The MM′Q resins thus obtained may react with organic or organosiloxane substances bearing olefin unsaturation (column 2, line

66 to column 3, line 3). Said patent also makes a vague and general allusion to supported acid catalysts (column 2, line 18).

Patent US-B-5 494 979 (≈ EP-A-0 617 094) discloses the preparation of MQ resins functionalized with acrylate radicals, by redistribution of polydiorganosiloxane oils bearing units D and units $D^{acrylate}$: $MD^{acrylate}_xD_yM$. This redistribution is performed using a xylene solution of commercial MQ resin, using triflic acid as preferred acid catalyst. The POS $MD^{acrylate}_xD_yM$ used is as described in example 2 of German patent 3 810 140. This preparation of acrylate-functionalized MQ resins also includes steps of neutralization, for example with sodium carbonate, and then of removal of the solid residues by filtration.

American patent US-B-5 510 430 concerns the functionalization of resins of MQ type with a whole range of functional groups, for example aryl, alkyl, vinyl or Si-H. The functionalization process used is based on the redistribution of disiloxanes. The examples more specifically disclose the redistribution of MQ resins of formula: $[(CH_3)_3SiO_{1/2}]_{0.65}[SiO_{4/2}]_1$ dissolved in toluene, by placing in contact with tetramethyldisiloxane and an acid catalyst that may be a phosphonitrile chloride, a linear phosphazene or triflic acid (example 6). This is therefore a redistribution MQ + M'$_2$ at the reflux temperature of the

solvent, with quenching of the reaction by using methanol, resulting in precipitation. Filtration and washing steps are then performed.

It emerges from this review of the prior art that the redistribution of MQ resins using functional oligo-organosiloxanes or functional polyorgano-siloxanes, in the presence of triflic acid derivatives, is not known.

Moreover, it appears that it would be entirely desirable to improve the known processes, especially in terms of functionalization yields and degrees of conversion of the POSs used for functionalization (M'_2).

Under these circumstances, one of the essential objects of the present invention is to provide an improved process for functionalizing silicone resins comprising siloxyl units M and Q, by redistribution using POSs bearing functional units or units for functionalization; this improved process needing to afford improvements in terms of ease of use, significant increase in the degree of functionalization of the redistributed resin and also of the degree of conversion of the functional POS reagents, while at the same time keeping the cost of the process as low as possible.

Another essential objective of the invention is to provide a new acidic catalytic system which is

useful or for the functionalization of silicone resins comprising units M and Q, by redistribution, using a redistribution reagent consisting of a POS bearing functional units or units for functionalization, said catalytic system having properties such that it allows an improvement in the redistribution kinetics and also in the yield and degree of conversion of the reaction, and does so without entailing any methodology complications or prohibitive cost increases.

Another essential objective of the invention is to significantly improve the homogeneous or heterogeneous catalysis of the reactions for functionalization of resins comprising siloxyl units M and Q by redistribution, using POSs bearing functional units or units for functionalization. The targeted improvement should be reflected in terms of the control, reliability and production efficiency of the corresponding industrial processes.

Another objective targeted through the improvement of the catalytic system is that of improving the quality of the functionalized MQ resins obtained, while at the same time optimizing the safety and minimizing the ecotoxic impact of the industrial processes under consideration.

Another essential objective of the invention is to provide a process for the functionalization of silicone resins MQ by redistribution, in which the

yield of incorporation of the POS for functionalization (M'_2) is significantly increased relative to those obtained by the known processes.

Another essential objective of the invention is to provide a process for the functionalization of silicone resins MQ by redistribution using POS for functionalization, which process offers the possibility of controlling the content of functionalities introduced and also the location of these functions on the resin.

Another essential objective of the invention is to propose a process for the functionalization of silicone resins of MQ type by redistribution, this process being able to be applied to a wide variety of chemical functions, so as to be able to produce a large variety of functional MQ resins adapted to a host of applications, from a starting material consisting of a resin core on the periphery of which are placed selected chemical functions.

These objectives, among others, are achieved by the present invention, which relates firstly to a process for preparing functionalized polyorganosiloxane (POS) resins comprising units M: ($R_3SiO_{1/2}$), Q: ($SiO_{4/2}$) and M': ($Y_aR_{3-a}SiO_{1/2}$) and optionally D: ($R_2SiO_{2/2}$) and/or D': ($RYSiO_{2/2}$) and T: ($RSiO_{3/2}$) and/or T': ($YSiO_{3/2}$),

with, in these units:

- the radicals R, which may be identical or

different, representing a C_1-C_{10} alkyl or a C_8-C_{12} aryl,

- the radicals Y being identical or different and representing a functional group Y,

by redistribution of POS resins using POSf bearing functional units M′ and/or D′ and/or T′, as defined above, in the presence of an acid catalyst,

said process being characterized in that at least one catalyst is used of formula (I) below:

$$\text{(I)} \quad (C_mF_{2m+1}SO_2)_nA$$

in which:

Δ m is an integer greater than or equal to 1;

Δ n is an integer equal to 1 or 2 and A represents NH_2 or NH with:

(i) n = 1 and A = NH_2 or NHR with R being a radical of SO_2-Z type with Z being a group other than C_mF_{2m+1}

(ii) n = 2 and A = NH.

It is necessary for the acid catalyst to be liquid under the working conditions. Furthermore, the choice of the catalyst may be guided by the gas-phase acidity scale described by I. Koppel et al., J. Am. Chem. Soc., 116 (1994) 3047. Thus, the acids used

should be those whose acidity measured in the gas phase is greater than that of sulfuric acid, thus, in terms of $\Delta G < 302$ Kcal/mol. For example, $(CF_3SO_2)_2NH$ $\Delta G = 292$ Kcal/mol, $(C_4F_9SO_2)_2NH$ $\Delta G = 284$ Kcal/mol.

It is thus seen that one of the essential constituent means of the invention concerns the catalytic system formed by three specific classes, (I)(i), (I)(ii) and (I)(iii), of triflic acid derivatives.

The use of this catalytic system makes it possible to obtain yields for incorporation of POSs bearing functional units (for example M'_2) of greater than 50%, preferably 60% and even more preferably 70%, to be compared with yields obtained in the processes according to the prior art having an upper limit of 30%.

The performance qualities obtained by virtue of this selection of triflic acid derivatives are entirely surprising and unexpected, not only in terms of yield of incorporation of POSf, but also as regards the degree of functionalization, i.e. the content of Si-function units in the resin MQ. Specifically, this degree is greater than 2.5% by weight and preferably greater than 3% in terms of the redistribution.

Moreover, the specifications of reduced cost, ease of use, safety and limited or even zero ecotoxicity are largely satisfied by the process

according to the invention.

The catalytic system according to the invention is also noteworthy in terms of kinetics.

Furthermore, the redistribution may be readily stopped by neutralization of the acid catalyst using a base (for example $NaHCO_3$, Na_2CO_3, $CaCO_3$, etc.) and/or by deactivation by heat.

The neutralization is all the more simple since the residual acidity in this case is markedly lower than that obtained after conventional redistribution catalysis. In addition, the neutralization has the advantage that the final reaction medium is not corrosive toward the functionalized MQ silicone resins. The stability of these resins with respect to temperature and storage is thereby greater.

Still regarding this stability aspect of the redistributed resin, it may also be pointed out that, since the catalytic system is present in trace amount in the reaction medium, it is nondegrading with respect to the products used and/or the products obtained after redistribution.

This process also makes it possible to control the degree of functionalization of the MQ resin, or even the location of its functions on the resin. Thus, starting with an MQ resin core, for convenience, it is possible to construct around this

core a functional peripheral structure, by customizing the morphology and hydrodynamic volume of the resin. For example, it may be envisaged to produce on the core hair made of POS segments of $(D)_x$ type.

According to one advantageous version a mixture of catalysts is employed comprising at least one catalyst of formula (I) as defined above and at least one catalyst of formula (I') below:

$$(I') \quad (C_mF_{2m+1}SO_2)OH$$

in which m is an integer greater than or equal to 1.

The functions that may be incorporated into the resin are, for example, of Si-H, Si-Vi, Si-phenyl, Si-alkyl, Si-alkenyl, Si-alkyne, Si-alkyl halide, Si-alkyl epoxide, Si-alkyl-polyether, Si-carbinol, Si-alkylammonium, Si-alkylcarboxylic acid or Si-alkylthiol type. It may thus be hoped to be able to provide functional resins adapted to a host of applications.

In point of fact, it may be envisaged to provide a tree produced from an industrial MQ-based resin.

Thus, the functions provided by the POSf are such that Y is advantageously chosen from the group comprising:

- hydrogen
- an alkenyl
- an alkynyl
- an aryl (preferably a phenyl)

- an (alkyl)epoxy
- an ether or a polyether
- a carboxylic acid
- an amide
- an amine
- a halide
- an alcohol
- a thiol or any other sulfur derivative.

In accordance with the invention, the starting MQ resins may be either unfunctionalized or already functionalized.

As regards the unfunctionalized MQ resins, they are commercial products, for example of formula $(M_xQ_y)_z$ with x between 0.5 and 1 and y between 0 and 1.

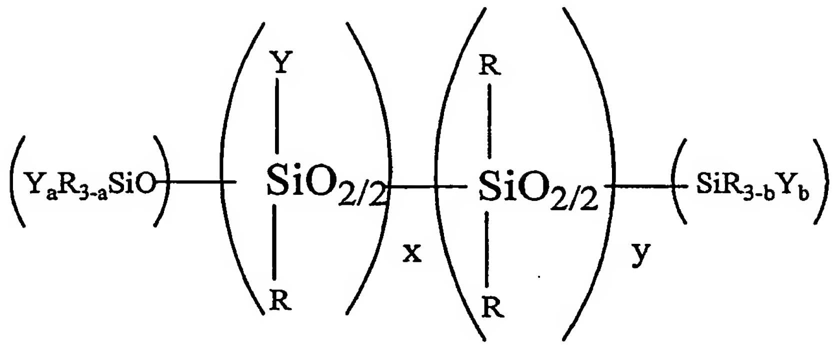
The already-functionalized MQ resins are especially those obtained by the process in accordance with the present invention from unfunctionalized starting MQ resins or by the synthetic process starting with sodium silicate described in patent US-2 676 182.

Advantageously, the starting MQ resin is in the form of a solution in an organic solvent, for instance xylene or toluene.

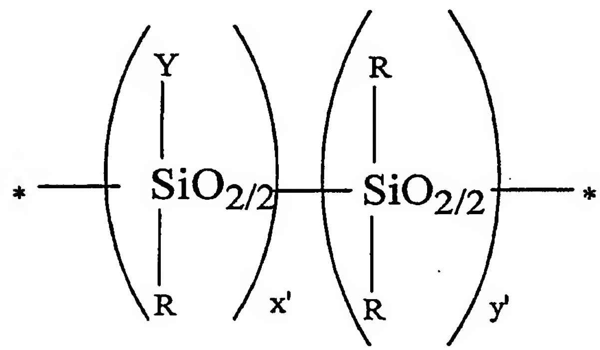
As regards the POSfs bearing functional units M′ and/or D′ and/or T′, which are useful for the redistribution, it will be preferred to use those of formula (IV.1), (IV.2) or (IV.3) below:

(IV.1): $(Y_aR_{3-a}Si)_2O$

(IV.2):



(IV.3)



in which:

- Y and R are as defined above,
- a and b = 0 to 2,
- $0 \leq x \leq 200$ and preferably $0 \leq x \leq 50$,
- $0 \leq y \leq 200$ and preferably $0 \leq y \leq 50$,
- with the condition that if $x + y = 0$, then a and/or $b \neq 0$,
- $1 \leq x' \leq 10$ and preferably $1 \leq x' \leq 8$,
- $0 \leq y' \leq 10$ and preferably $0 \leq y' \leq 3$,
- $3 \leq x' + y' \leq 10$ and preferably $x' + y' = 3$,

4 or 5.

The POSfs of formulae (IV.1), (IV.2) and (IV.3) correspond, respectively, to disiloxanes, linear polyorganosiloxanes and cyclic oligoorganosiloxanes.

These POSfs are, for example, M_2, M_2^{Vi}, MD_xM, $MD_xD'_yM$, $M'D_xD'_yM'$, $MD_xD^{Vi}{}_yM$, $M^{Vi}D_xD^{Vi}{}_yM^{Vi}$, $M'D_xM'$, $M^{Vi}D_xM^{Vi}$, $D_{x'}{}^{Vi}D_{y'}$.

It should be noted, as regards the acid catalyst of formula (I)(i) or (ii) or (iii) that the fluoro chain C_mF_{2m+1} may be extended so as to increase the acidity of the catalyst and subsequently its efficacy.

In practice, the acid catalysts may be, for example:

I(i) n = 1 and A = OH

I(ii) n = 1 and A = NH2 or NHR with R being a radical of SO_2-Z type with Z being a group other than C_mF_{2m+1}

I(iii) n = 2 and A = NH.

The chosen catalyst preferably has a melting point lower than the reaction temperature, so that the catalyst is in the liquid state during the reaction.

In the preferred embodiment of the process according to the invention, the catalyst is trifluoromethanesulfonimide acid of formula (I)(ii) with m = 1 and A = NH2.

In quantitative terms, it may be pointed out

that the concentration of acid catalyst (I) is advantageously between 1 ppm and 2% relative to the starting resin. Moreover, the catalyst (I)/inert support (preferably carbon black) mass ratio is preferably between 0.1 and 10, and is preferably of the order of 1.

In accordance with the invention the catalysis may be homogeneous or heterogeneous. It is preferably homogeneous, the catalyst being in this case dissolved in the reaction medium.

According to a variant of heterogeneous catalysis, the catalyst is at least partially absorbed onto an inert support which may be, for example, carbon black or silica.

The process according to the invention may be defined by other methodological characteristics, and in particular in that it comprises the following essential steps:

1- combining the starting POS resin, the POSf bearing functional units, the acid catalyst (I) - optionally supported - in an organic solvent;

2- reacting preferably at a temperature θr greater than or equal to room temperature and less than or equal to the boiling point of the solvent, and even more preferably between 50°C and 100°C;

3- optionally quenching the reaction by adding an agent for neutralizing the acid catalyst (I);

4- optionally removing the supported acid catalyst (I) from the reaction medium, preferably by filtration.

Advantageously, as has already been mentioned above, the organic solvent, preferably xylene and toluene, is provided in the reaction medium by means of a solution of starting POS resin (MQ) in said solvent. It is also possible to work with an excess of functionalized silicone oil.

The process of functionalization by redistribution according to the invention makes it possible especially to graft Si-H and/or Si-alkenyl (preferably vinyl) units onto MQ resins. Given that these functions H or alkenyl are reactive functions, among others, it may be envisaged, in accordance with the invention, to perform a second functionalization according to a hydrosilylation mechanism, so as to covalently attach a second functional segment onto the already functionalized MQ resin.

This corresponds to the case in which Y represents H or alkenyl in the functional units M′ and/or D′ and/or T′, of the POSf. In this variant, after the redistribution, other functionalization radicals Y_1 bearing at least one unsaturation

(preferably ethylenic) or at least one Si-H unit are grafted onto the ≡Si-H or ≡Si-alkenyl units, respectively, of the redistributed resin.

As regards the methodology, it may also be pointed out that it is preferable, in order for the redistribution to proceed correctly, for the reaction atmosphere to be free of moisture. Thus, the process is advantageously performed under an atmosphere of neutral gas, for example argon or nitrogen.

The reaction pressure is advantageously normal and the reaction temperature may range from room temperature (for example 25°C) to a temperature of 150°C or more.

The redistribution is stopped by means of deactivating the catalyst. Since it is an acid catalyst, in this instance triflic acid or derivatives thereof, the deactivation may be performed using a basic neutralizer, for instance sodium carbonate Na_2CO_3 or sodium bicarbonate $NaHCO_3$.

The neutralization is all the more necessary when the catalysis is homogeneous catalysis, since, in such a case, in contrast to heterogeneous catalysis, the catalyst is not removed at the end of the reaction.

According to one variant of the process in accordance with the invention, the redistributed and functionalized resin obtained is subjected to at least one other redistribution/functionalization, using POS

bearing functional units.

The invention also relates to a catalytic system that is useful for preparing functionalized polyorganosiloxane (POS) resins comprising units M: $(R_3SiO_{1/2})$, Q: $(SiO_{4/2})$ and M': $(Y_aR_{3-a}SiO_{1/2})$ and optionally D: $(R_2SiO_{2/2})$ and/or D': $(RYSiO_{2/2})$ and/or T: $(RSiO_{3/2})$ and/or T': $(YSiO_{3/2})$ with, in these units:

- the radicals R being identical or different and representing a C_1-C_{10} alkyl or a C_8-C_{12} aryl;
- the radicals Y being identical or different and representing a functional group Y, preferably chosen from the group comprising:
  - hydrogen
  - an alkenyl
  - an alkynyl
  - an aryl (preferably a phenyl)
  - an (alkyl)epoxy
  - an ether or a polyether
  - a carboxylic acid
  - an amide
  - an amine
  - a halide
  - an alcohol
  - a thiol or any other sulfur derivative

by redistribution of POS resins using POSs bearing functional units M' and/or D' and/or T' as defined

above,
characterized in that it comprises at least one catalyst of formula (I) below:

$$\text{(I)} \quad (C_mF_{2m+1}SO_2)_nA$$

in which:

- Δ m is an integer greater than or equal to 1;
- Δ n is an integer equal to 1 or 2 and A represents OH, NH_2 or NH with:
  - (i) n = 1 and A = NH_2 or NHR with R being a radical of SO_2-Z type with Z being a group other than C_mF_{2m+1}
  - (ii) n = 2 and A = NH
  - (iii) n = 1 and A = OH.

This catalytic system is markedly more efficient than the conventional catalysts for the redistribution of silicone resins MQ using only TFOH. In terms of kinetics, conversion and yield, it makes it possible to obtain high-quality functionalized MQ resins, the functionality of which is controlled and adapted to the intended use. These performance qualities are all the more advantageous since they are obtained without sacrificing the imperatives of cost, safety, absence of ecotoxicity and ease of use.

The examples that follow will make it

possible to understand more clearly the process and the catalyst according to the invention, by highlighting all their advantages and the possible implementation variants.

EXAMPLES

I - Comparative example - Tonsil catalyst:

500 g of a xylene solution containing 300 g of resin $(M_xQ_y)_z$ (structure determined by ^{29}Si NMR: $(M_{0.88}M'_{0.06}D^*_{0.05}Q_1^*)_{z}$- M/Q = 0.9) are introduced into a 1 liter reactor under nitrogen. 30 g of M'_2 (1.49 mol SiH/kg) and 2.7 g of Tonsil are added. The mixture is brought to 70°C and heated at this temperature for 7 hours. After cooling to room temperature, the reaction mass is filtered through cardboard and then through a 0.45 µm PTFE filter to remove the Tonsil. During the test, several samples are taken and make it possible to monitor the amount of SiH bound to the resin and also the nature and relative proportions of the light fractions in the reaction medium as a function of the reaction time.

TABLE 1

Reaction time	0 h	1 h	3 h	6 h	7 h
Amount of SiH on the resin (quantification by IR)	0%	0.8%	1.2%	1.47%	1.39%
Conversion of M'_2 (quantification by GC)	0%	52%	74%	78%	82%

Final structure of the resin (^{29}Si NMR):

$(M_{0.82}M'_{0.08}D^*_{0.05}Q_1{}^*)_z$

Final yield of incorporation of SiH: 32%.

II - Comparative test - Tonsil catalyst:

500 g of a xylene solution containing 300 g of resin $(M_xQ_y)_z$ (NMR analyses: $(M_{0.9}D^*_{0.02}Q_1)_z$ with M/Q = 0.9 (molar)) are introduced into a 3 liter reactor under nitrogen. This solution is brought to 70°C and 30 g (1.49 mol SiH/kg) of M'_2 and 2 g of Tonsil are added. The mixture is left to react for 7 hours at 70°C. The reaction mass is cooled and filtered through cardboard + 0.45 µm PTFE filter to remove the Tonsil. During this test, a certain number of samples are taken, which make it possible to monitor the amount of SiH units as a function of time:

T=0: 0%, T=1h: 0.8%, T=3h: 1.2%, T=7h: 1.47%, or 1.39% (IR), i.e. 0.48 mol SiH/kg of resin.

The yield for incorporation of the SiH units is 32%. The NMR analyses show that the structure of the final resin is: $(M_{0.8}M'_{0.07}D^*_{0.04}Q_1)_z$.

III - Comparative example - CF_3SO_3H catalyst:

The operating conditions are the same as those described in example I.

Materials added: 500.0 g of xylene solution, i.e. 300 g of resin

30.0 g of M'_2, i.e. 1.47 mol/kg

1.31 g of CF_3SO_3H

Reaction time: 7 hours

Monitoring of the reaction:

TABLE 2

Reaction time	0 h	1 h	3 h	6 h	7 h
Amount of SiH on the resin (quantification by KOH assay)	0%	2.79%	3.17%	3.08%	3.28% 3.37% (I)
Conversion of M'_2 (%) (quantification by GC)	0%	94.5%	97%	97%	97%

Final structure of the resin (^{29}Si NMR):

$(M_{0.72}M'_{0.11}D^*_{0.04}Q_1{}^*)_z$

Final yield of incorporation of SiH: 75%.

IV - Example - $CF_3SO_2)_2NH$ catalyst:

The operating conditions are the same as those described in example I.

Materials added: 500.3 g of xylene solution, i.e. 310 g of resin

31.6 g of M'_2, i.e. 1.49 mol/kg

2.46 g of TFSI

Reaction time: 6 hours

Monitoring of the reaction:

TABLE 3

Reaction time	0 h	1 h	3 h	6 h
Amount of SiH on the resin (quantification by KOH assay)	0%	2.87%	3.23%	3.04% 3.30% (IR)
Conversion of M'_2 (%) (quantification by GC)	0%	95%	97%	97%

Final structure of the resin (^{29}Si NMR):

$(M_{0.74}M'_{0.11}D^*_{0.04}Q_1{}^*)_z$

Final yield of incorporation of SiH: 76%.

V - TFSI catalysis test:

Same operating conditions as for example I:

- 500 g of xylene solution containing 300 g of resin M_xQ_y
- 30 g of M'_2, i.e. 1.49 mol of SiH/kg of resin
- 2.46 g of TFSI

⇒ reaction time: 7 hours ➔ IR assay: 1.05%, mol SiH/kg of resin

SiH assay after 1 hour reaction : 1.07 mol SiH/kg, 3 hours: 1.03 mol SiH/kg of resin

⇒ yield of SiH incorporation: 70%

⇒ final resin structure: $(M_{0.7}M'_{0.12}D^*_{0.05}Q_1)_z$

VI - CF_3SO_3H catalysis test

Same operating conditions as for example I:

- 642.1 g of xylene solution containing 400 g of resin $(M_xQ_y)_z$
- 47.21 g of $M^{Vi}{}_2$, i.e. 1.27 mol of Si-vinyl/kg of resin
- 2.45 g of carbon black
- 1.71 g of CF_3SO_3H

⇒ reaction time: 8 hours 10 minutes ➔ IR assay: 1.1 mol Si-vinyl/kg of resin

⇒ yield of SiH incorporation: 87%

⇒ final resin structure: $(M_{0.76}M^{Vi}{}_{0.11}D^*{}_{0.03}Q_1)_z$.